

Title: Formation and Fate of SO₃ During Combustion of Petroleum Coke

Author: Jay R. Gunderson
jgunderson@eerc.und.nodak.edu
Telephone: (701) 777-5258
Fax: (701) 777-5181
Energy & Environmental Research Center
PO Box 9018
Grand Forks, ND 58202-9018

Summary

The sulfur in petroleum coke occurs in various compounds, e.g., elemental sulfur, hydrogen sulfide, mercaptans, disulfides, thiophenes, and thiophanes, while vanadium occurs primarily in organometallic porphyrins. During combustion, sulfur species are converted to SO₂ and, to a lesser extent, SO₃. Vanadium is converted to a number of oxide states, including V₂O₅, vanadium pentoxide. Although all other oxidation states of vanadium are refractory in nature (melting points greater than 3500°F), V₂O₅ melts at only 1274°F and is a very effective oxidation catalyst. The amount of vanadium in petroleum coke varies from region to region throughout the world and is a function of the vanadium content of the crude and the efficiency of the refining process. In a pulverized coal-fired unit, vanadium pentoxide can have a significant impact on the amount of SO₃ present in the flue gas and adsorbed on fly ash grains.

Laboratory- and pilot-scale tests were performed to determine the operating parameters affecting the formation of vanadium-catalyzed SO₃ and its effect on air heater deposition, baghouse operation, and transport in a pneumatic, fly ash-handling system. On three separate occasions between 1992 and 1994, a high-vanadium-content petroleum coke was fired in a pilot-scale test furnace. Tests were performed in support of design activities by a boiler vendor to safely fire the petroleum coke to produce process steam for refinery operations. Over the course of the first two tests, it was noted that a significant portion of the vanadium in the fly ash was converted to V₂O₅, and increased concentrations of SO₃ were present in the flue gas and as adsorbed species on fly ash grains. Because the increased SO₃ concentrations can be detrimental to system operations in the low-temperature regions of the boiler and ash-handling systems, a third test was conducted to investigate the use of a calcium sorbent to minimize the deleterious effects of SO₃ and acidic fly ash. An in situ acid dewpoint meter and extractive sampling were used to quantify SO₃ concentrations at the baghouse inlet and exit.

Results of testing indicated that catalytic oxidation of SO₂ to SO₃ by vanadium pentoxide present in the fly ash occurred throughout the combustion system, with SO₃ concentrations as high as 158 ppm measured at the baghouse inlet. Normal combustion conditions generally promote the formation of SO₃ at between 1% and 2% of the flue gas SO₂ concentration, which corresponds to between 16 and 32 ppm based on input sulfur concentrations for the petroleum coke tested here. Laboratory tests indicated that catalytic oxidation would occur at temperatures as low as the design baghouse operating temperature of 335°F, with the highest conversion rates

evident at temperatures exceeding 650°F. Furthermore, fly ash analyses indicated significant levels of adsorbed SO_3 in addition to particulate sulfates and sulfate hydrates, indicating even higher conversion rates of SO_2 to SO_3 . These acidic fly ash species are readily hydrated when exposed to ambient conditions, converting the golden fly ash to a blue–green color as the hydration occurs to a black color when hydration is complete and the ash dries. The pH of this ash was measured with litmus paper at about 1. The moisture absorption creates a very corrosive fly ash that pitted the surfaces of stainless steel heat exchange surfaces after cooling. Laboratory experiments indicated that at temperatures above 160°F, essentially no moisture is absorbed by the fly ash. For this reason, it was recommended that the pneumatic fly ash-handling system be designed to maintain surface metal temperatures above 160°F.

Also of concern was the air heater system for the full-scale installation. To investigate fouling and corrosion of these surfaces, a simulated tubular air heater was constructed and inserted into the duct at design inlet temperatures ahead of the baghouse inlet. Results indicated that hard deposits were formed over a very short time period, but quickly reached a steady-state thickness without plugging flue gas passages. The ash on these surfaces had begun hydration as indicated by the blue–green color at the tube surface. The vendor retained these probes for in-house determination of corrosion.

The acidic fly ash and the high acid mist concentration entering the baghouse created considerable concern for the integrity of the baghouse construction materials. In an effort to sorb the incoming SO_3 species, hydrated lime was used as a precoat on the fabric filters, with periodic injection of hydrated lime. Results indicated that the precoat was effective in reducing the acid mist concentration leaving the baghouse to within acceptable limits. In addition, it was determined that use of an in situ acid dewpoint meter located at the baghouse exit could be used to establish breakthrough of the acid mist and trigger duct injection of hydrated lime.